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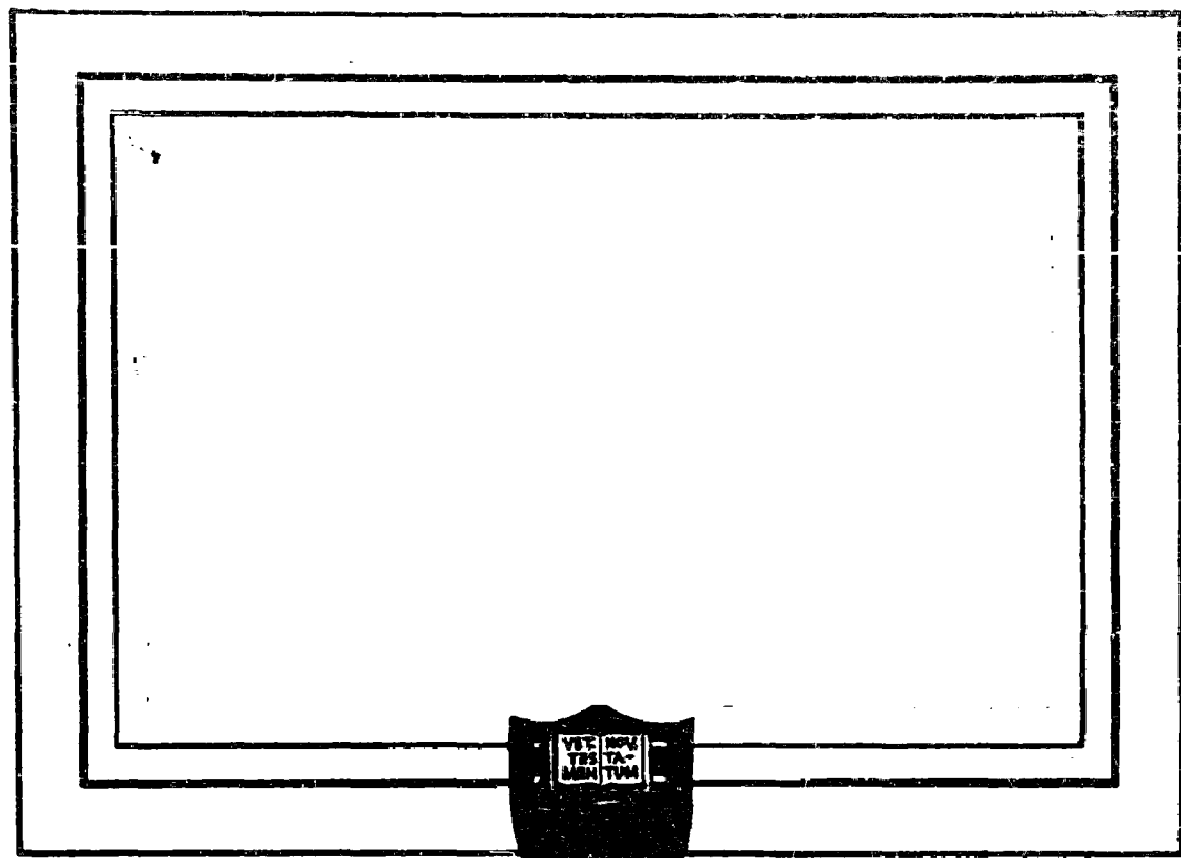
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INVESTIGATION OF THE PHOTOELECTRIC
WORK FUNCTION OF TITANIUM

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August 1952

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Office of Naval Research
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SUMMARY

Equipment consisting essentially of a continuously variable monochromatic ultra-violet light source and a sensitive detecting system for measuring photoelectric emission was constructed. Two photocells employing pure titanium cathodes, one plane and the other semi-cylindrical, were made, and measurements of relative photoelectric response versus incident light frequency were recorded for several different temperatures. After normalizing the incident light intensity by means of measurements taken with a calibrated phototube, conventional Fowler plots were made for each temperature and compared with the theoretical curve. The experimental curves gave good fit with the theoretical curve and the value of photoelectric work function was computed in each instance.

The results from the first tube yielded a mean value of 4.50 volts for the photoelectric work function of pure titanium for seven different temperature runs with deviation from the mean no greater than approximately $\pm 1\%$ for any individual run. The second tube produced a mean value of 4.11 volts, the maximum deviation from the mean value being within $\pm 1\%$ for four different temperature runs.

The experimental results lead to the conclusions that the photoelectric work function of pure titanium is 4.11 volts, the higher value obtained from Tube I being caused by a slight contamination of the titanium cathode surface, and that contamination of the titanium cathode produces a change in work function that may cause it to increase or decrease. Difficulties encountered due to cathode contamination are described.

I INTRODUCTION

A great deal of interest has been exhibited recently toward the investigation of the work functions of zirconium and titanium, both in pure form and with oxygen and nitrogen added. It was hoped that these investigations would possibly lead to the discovery of a practical emitter possessing the desirable qualities of high emission efficiency and negligible effect due to positive ion bombardment.

In 1932, Rentschler, Henry, and Smith¹ reported a series of experiments concerning the photoelectric responses of several pure metals among which zirconium and titanium were included. Specially prepared photocells containing cathodes upon which the pure metals were deposited by a sputtering process were used. In 1945, Rentschler and Henry² found that the effect on the photoelectric threshold of both zirconium and titanium following the absorption of certain amounts of oxygen and nitrogen was that of shifting the threshold to longer wavelengths in every case. They also found that this shift was not caused by a surface layer effect, but rather by a volume effect.

In 1950, Wahl³ concluded from the results of thermionic emission measurements that the work function of zirconium manifests a tendency to decrease as oxygen is added up to a certain amount, and then it begins to rise upon further addition of oxygen. He also found that this increase in thermionic emission caused by the oxygen in solution is not affected appreciably by positive ion bombardment. However, the work function of zirconium with the optimum amount of oxygen added still leaves it a less efficient emitter than tungsten.

In 1952, Robinson⁴ observed the effect on the thermionic work

function of titanium after the absorption of varying amounts of oxygen and found that it behaves similar to zirconium in that the work function decreases to a minimum value upon increasing the oxygen content and then begins to rise slightly as further oxygen is added. This minimum value still leaves titanium as an even poorer emitter than zirconium.

This paper reports the results of experimental work whose purpose has been the buildup of a suitable photoelectric detecting system and associated ultra-violet light source, and the measurement of the photoelectric work function of pure titanium. It is intended as the first step of an investigation of the effect of oxygen absorption on the photoelectric work function of titanium which will be conducted in the future in order to determine whether or not photoelectric measurements corroborate the conclusions derived from the thermionic experiments performed by Robinson.

II THEORY

The work of R. H. Fowler^{5,6,7} has indicated that the effect of temperature on photoelectric emission is of considerable importance both in explaining the shift in the "apparent" threshold frequency with temperature and in providing a convenient method of determining the photoelectric work function of metals. Use is made of the fact that at all temperatures other than zero degrees K., the Fermi distribution function for electrons in metals theoretically approaches the energy axis asymptotically. Thus, there is no distinct "threshold" except at absolute zero, and the term as usually defined loses its quantitative significance. Fowler defines the "true" photoelectric threshold ν_0 from the equation

$$h \nu_0 = W_a - \mu = \phi \quad ,$$

where; h = Planck's Constant

W_a = surface potential energy barrier

μ = maximum energy of an electron in the metal at zero deg. K.

ϕ = photoelectric work function

Fowler assumes that the photoelectric emission current I from a surface at temperature T by light of frequency ν which is close to ν_0 is proportional to the number of electrons per unit volume within the metal which have a velocity component ξ normal to the surface which is greater than the critical value ξ_0 , such that

$$\frac{1}{2} m \xi_0^2 + h \nu = W_a \quad ,$$

and that the electrons within a metal obey the Fermi-Dirac statistics. He proceeds to calculate this number of "available" electrons from the Fermi velocity distribution function and derives the expression

$$\log(I/T^2) = B + \log f(x) ,$$

where; $B =$ a constant independent of ν and T

$$x = [\frac{h\nu - \phi}{kT}]$$

and $f(x)$ is a universal function of x which has the same form for all metals and all temperatures.

If the theoretical curve $\log f(x)$ as a function of x is plotted, and the experimental values of $\log(I/T^2)$ versus $(h\nu/kT)$ for one particular temperature plotted on the same set of coordinate axes, as in Figure 1, it is seen that the two curves are identical but are displaced from one another both vertically and horizontally. If the experimental curve is shifted until it coincides with the theoretical curve, the vertical displacement is a measure of B and is unimportant, but the horizontal displacement is a measure of ϕ / kT , and thus the photoelectric work function can be determined since T is known.

Although the Fowler equation was developed for the condition where ν is near ν_0 , it has been found⁸ that accurate experimental results can be obtained for values of ν which differ from ν_0 by as much as 30 per cent.

An alternate method of plotting Fowler's equation which possesses certain experimental advantages over the above method has been developed by DuBridge⁸. Instead of plotting $\log f(x)$ as a function of x , it is plotted as a function of $\log x$ (for $x > 0$). This results in a curve

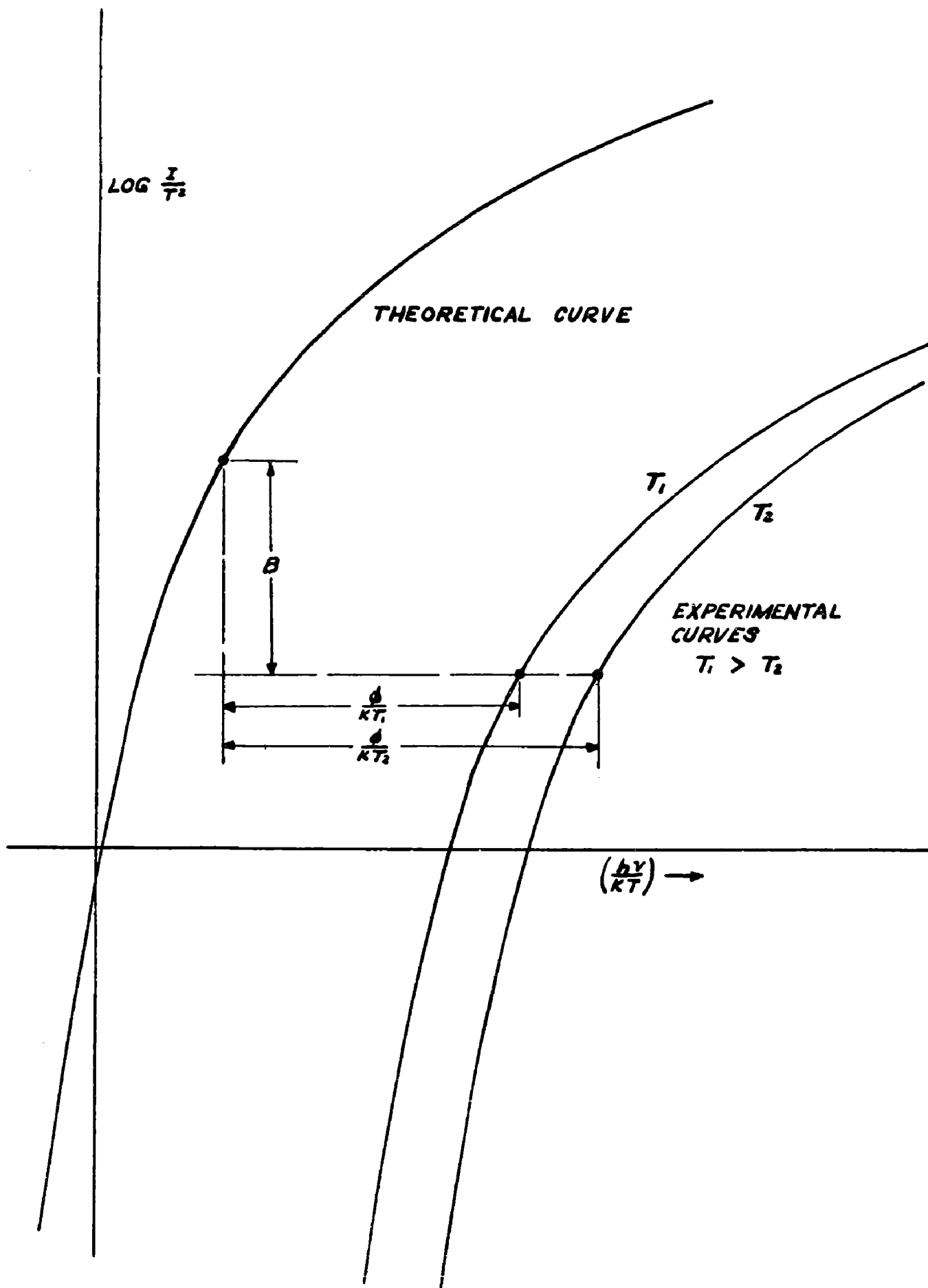


FIGURE 1

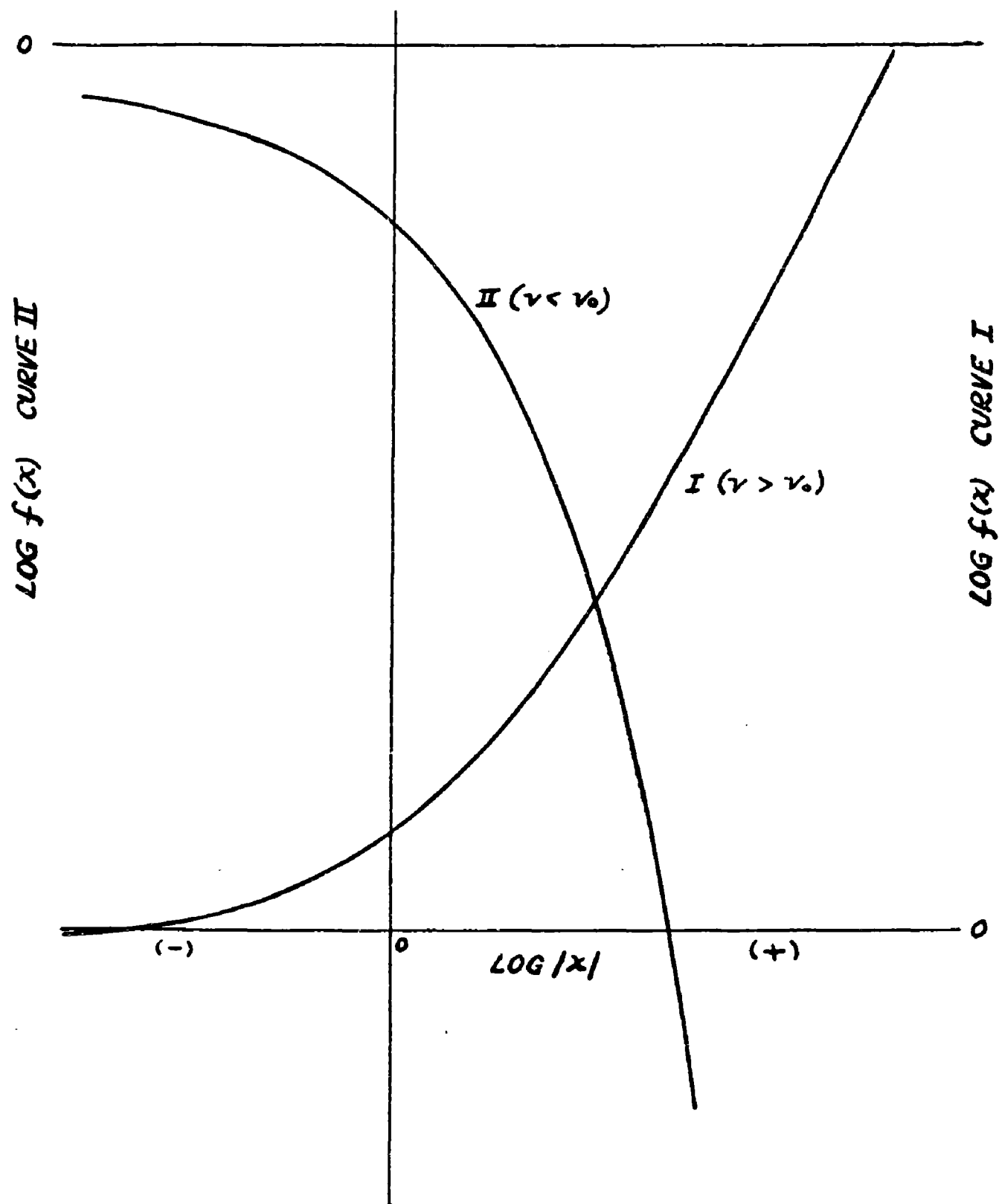


FIGURE 2

which is concave upward, as shown in Figure 2, and approaches the horizontal for large negative values of $\log x$. If observations are taken at a given incident frequency ($\nu > \nu_0$) of the photoelectric yield as a function of the temperature, the resulting plot of $\log(I/T^2)$ versus $\log(1/T)$ is found to be an "isochromatic" curve of the same shape as the concave upward theoretical curve. If these two curves are plotted on the same set of coordinate axes, the vertical shift necessary to bring them into coincidence is a measure of B as before and therefore gives no pertinent information. The horizontal component of shift is equal to $\log\left[\frac{h(\nu - \nu_0)}{k}\right]$, since from the definition of x ,

$$\log x = \log\left[\frac{h(\nu - \nu_0)}{k}\right] + \log(1/T) \quad .$$

Thus, from measurements taken at a single known frequency, it is possible to determine ν_0 and thence ϕ . This method offers the advantage that the relative intensity of the light at various frequencies need not be known since normalizing I only introduces a certain amount of vertical shift to the experimental curves.

If observations are taken for $\nu < \nu_0$ ($x < 0$), the theoretical curve is obtained by plotting $\log f(x)$ against $\log(-x)$. This curve is shown also in Figure 2. However, since the values of photocurrent obtained for $\nu < \nu_0$ are small, better results are obtained for frequencies above the threshold.

Since sections of both theoretical curves are practically linear, it is possible to plot experimental data which yield no significant results, since it is impossible to match two linear portions of the curves with any degree of accuracy. In order to obtain data which will

fall on the curved portions, observations should be made for low temperatures and frequencies away from the threshold for the "isothermal" method; for the "isochromatic" method, measurements should be taken for high temperatures and frequencies near ν_0 .

Experimental tests^{8,9,10} of the Fowler theory employing both methods have indicated it to be a very accurate and experimentally feasible method of measuring photoelectric work function.

III EXPERIMENTAL PROCEDURE

1. Construction

Photocells

Two special photocells were constructed for the experiments on pure titanium. These shall henceforth be referred to as Tube I and Tube II. Constructional features of Tube I are shown in Figure 3. The envelope is composed of a spherical Pyrex shell with a cylindrical quartz optical window attached at one point and a base stem diametrically opposite. The anode consists of a thin gold film which was evaporated on the inside of the spherical envelope before the quartz tube and base stem were attached. This was accomplished by inserting a tungsten solenoid which supported small chunks of gold into the spherical envelope through the base stem opening and then passing a current through the tungsten in order to heat it. When the temperature of the tungsten exceeded the melting point of gold the chunks of gold became molten, and the gold distributed itself over the tungsten surface due to the action of surface tension. Upon further heating the gold evaporated and deposited in a thin film on the cooler glass inner surface. A phosphor-bronze strip pressing against the gold connects it electrically to the external anode connection through a tungsten-to-glass seal.

The cathode is a plane rectangular sheet, .002 inch in thickness, of pure titanium[#] spot welded to nickel supporting rods. The plane of the cathode is oriented normal to the path of the light beam entering through the quartz window. A chromel-alumel junction thermocouple is

[#] Obtained from Foote Mineral Company, Philadelphia, Pa.

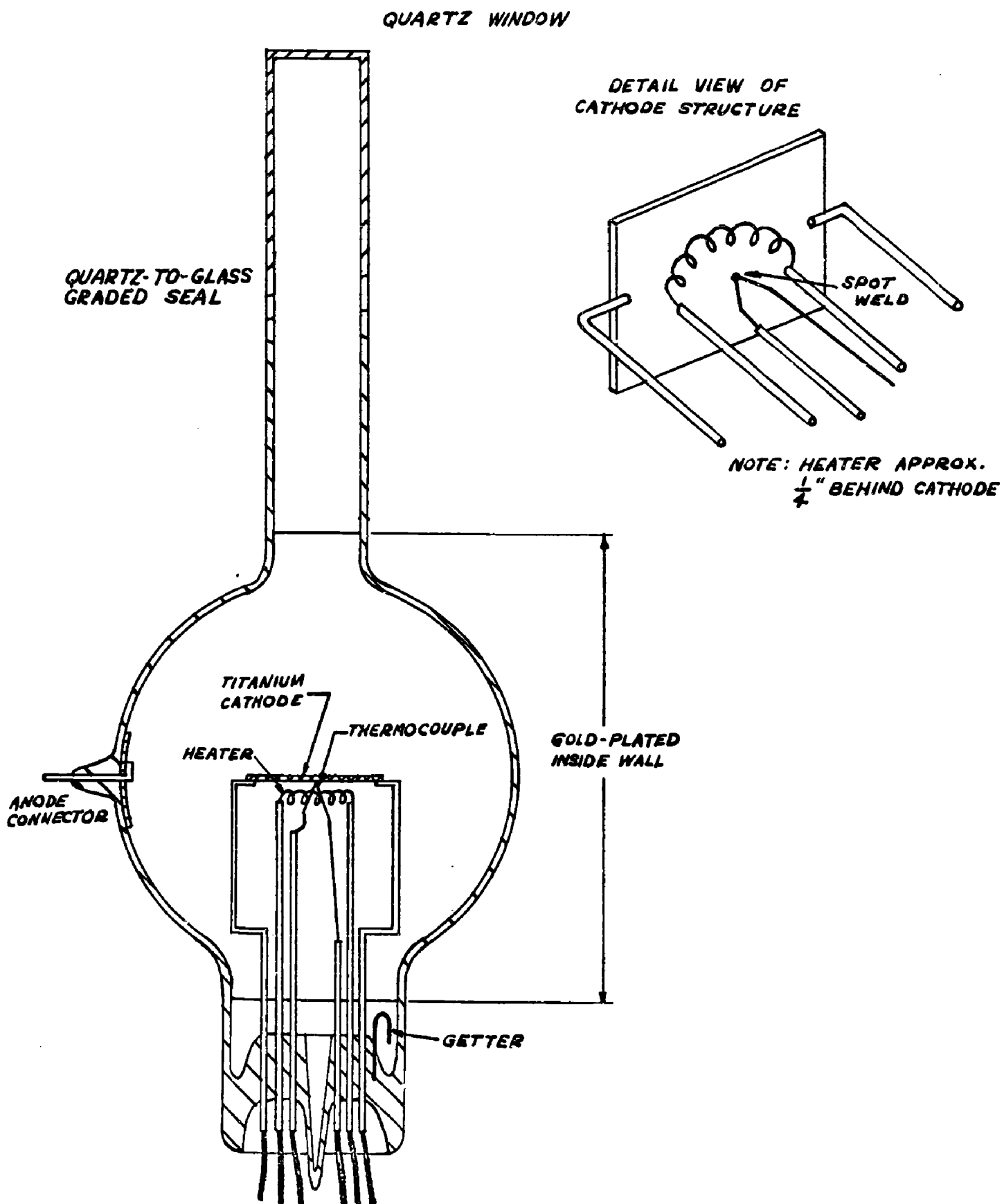


FIGURE 3 - TUBE I

attached directly to the back of the cathode to make possible cathode temperature measurements. A tungsten heater wound in the form of a spiral is mounted directly behind the cathode; this facilitates making measurements with the cathode at various temperatures. All elements are connected to external leads by tungsten-to-glass seals.

The fused quartz optical window tube was attached by means of a graded quartz-to-glass seal. Next, the base stem containing all internal elements and supporting members which were previously thoroughly cleaned with acetone, ethyl alcohol, and finally distilled water was connected to the spherical shell, and the complete tube was sealed to a mercury diffusion pump through a small tip-off tube in the center of the base stem. The tube was pumped continuously for 24 hours at room temperature, then baked at 400 degrees C. for 6 hours by means of an oven surrounding the tube while the pumping continued. This baking process served to outgas the metal parts and the glass inner surface. After removing the oven, pumping was continued at room temperature for several hours until the pressure as measured with an ionization gauge connected in the vacuum system reached 10^{-7} mm of Hg at which time the getter consisting of a loop of tungsten coated with batalum was evaporated by means of R.F. induction heating and the tube immediately sealed off from the pump.

A coating of aquadag was applied to the outer surface of the glass extending from the base stem almost to the end of the quartz window tube; when connected to ground, this prevents the sporadic buildup of electrostatic charges on the outside glass surface which have a tendency to produce noise in the photocell output.

Constructional details of Tube II are depicted in Figure 3a. The

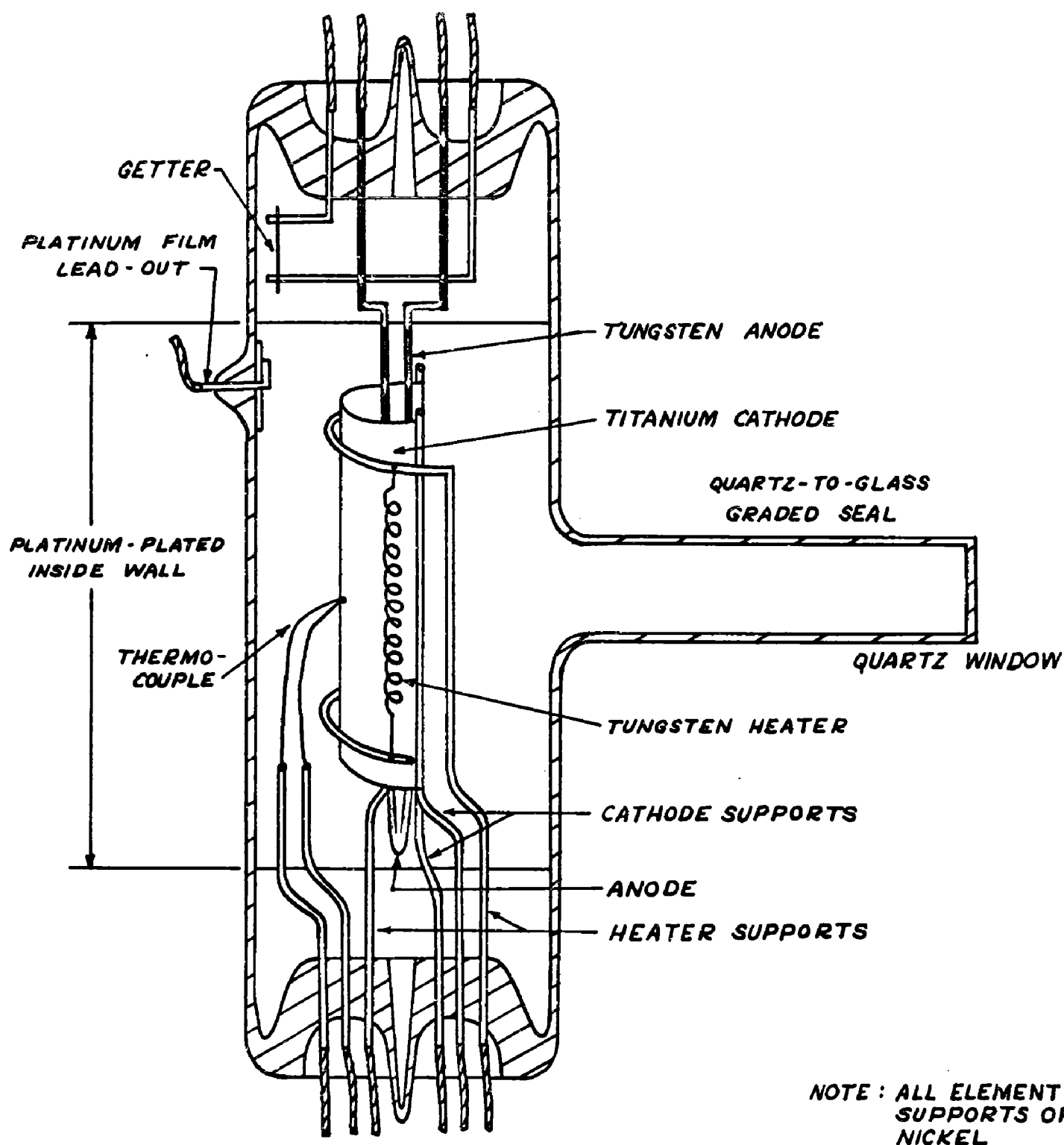


FIGURE 3a - TUBE II

gold film anode and plane titanium cathode features of Tube I were discarded in favor of a simpler system consisting of a semi-cylindrical cathode and "hairpin" loop anode. The looped anode construction provides more rigid support than a single wire and permits the anode to be well outgassed by passing current through it. The semi-cylindrical cathode was shaped from a rectangle cut from the same sheet of pure titanium which furnished the cathode for Tube I. A chromel-alumel junction thermocouple was again spot welded directly to the back side of the cathode. The heater is composed of two spirals wound from tungsten wire, connected electrically in parallel, and mounted approximately 1/8 inch behind the cathode. Figure 3a shows clearly how one of the spirals, extending in the direction of the cylindrical axis of the cathode, is supported by nickel rods behind one side of the cathode; the other spiral is symmetrically located on the opposite side of the cathode structure. A fused quartz optical window identical to the one employed for Tube I was attached directly in front of the cathode to allow the incident light to impinge on the cathode.

An early version of Tube II employed an aquadag inner coating to prevent sporadic buildup of electrostatic charges and an auxiliary connected tube containing six tantalum wire getters. This tube gave very poor photoelectric results and upon inspection the cathode was found to be badly contaminated. It was suspected that impurities given off by the tantalum which required heating to a white-hot temperature before finally evaporating and the aquadag which unavoidably became heated due to its proximity to the heater spirals caused the cathode contamination. Therefore, those were eliminated in the final version, being replaced by a tantalum strip getter and a platinum film, respectively.

The platinum was painted on the inside wall of the glass envelope before the elements were mounted and fired at 600 degrees C. for approximately 3 hours. A separate lead-out connection is provided on the side of the tube in order to allow for the connection of the platinum to the anode during operation. This arrangement was found to produce better results than directly grounding the platinum.

A different pumping procedure was used for Tube II. After the metal parts were thoroughly cleaned and mounted inside the envelope, the tube was sealed to a mercury diffusion pump and pumped at room temperature for half an hour. Then it was covered with an oven and pumped and baked at 450 degrees C. continuously for 30 hours at which time the pressure was measured as approximately 10^{-7} mm of Hg by an ionization gauge in the vacuum system. The oven was removed and the baterialum getter evaporated by passing current through it; the tube was then immediately sealed off from the pump.

Light Source, Monochromator, and Tube Setup

After careful consideration of several light sources which give usable radiation down to at least 2400 Å, it was decided to use a General Electric A-H6 high-pressure mercury arc lamp. Although the spectral energy distribution of this unit is far from being constant over an appreciable range of frequencies, the intensity of radiation in the interval from 3000 Å to 2400 Å is much greater than for other mercury and hydrogen radiation sources considered. Maximum obtainable intensity of the incident light is a prime requisite for these measurements since the reflectivity of titanium is comparatively high, therefore the photoelectric yield is rather low. The A-H6 lamp is

mounted in a quartz water-cooling jacket which prevents the temperature of the arc from becoming excessive. It is operated from a 1000 volt alternating current power supply consisting primarily of a 60 cycle high voltage step-up transformer.

The non-uniform nature of the spectral energy distribution of the light source requires a calibration of light intensity throughout a range of frequencies when photocurrent measurements are taken as a function of frequency. Fortunately, it is not necessary to determine absolute values of light intensity since only relative values are needed. This is due to the fact that as mentioned earlier, normalizing the photocurrent only contributes a vertical shift to the Fowler plot thereby affecting the constant term B solely. The calibration of the spectral intensity distribution was accomplished using a calibrated phototube; this procedure is described in more detail in a later section.

The light energy was dispersed with a Perkin-Elmer model 83 monochromator which employed a fused quartz prism and front surface reflecting mirrors. The wave-length vernier of this instrument is calibrated in scale divisions which must be transformed into Angstrom units by means of a calibration chart. A calibration curve prepared for an identical monochromator also using a fused quartz prism was obtained from Dr. H. B. DeVore¹¹, and our unit was checked against this curve using the line spectra from a low-pressure mercury arc source. The checks proved to be within the resolution width of the instrument, therefore this calibration chart was accurately traced and employed for the measurements on titanium.

¹¹ RCA Research Laboratories, Princeton, New Jersey

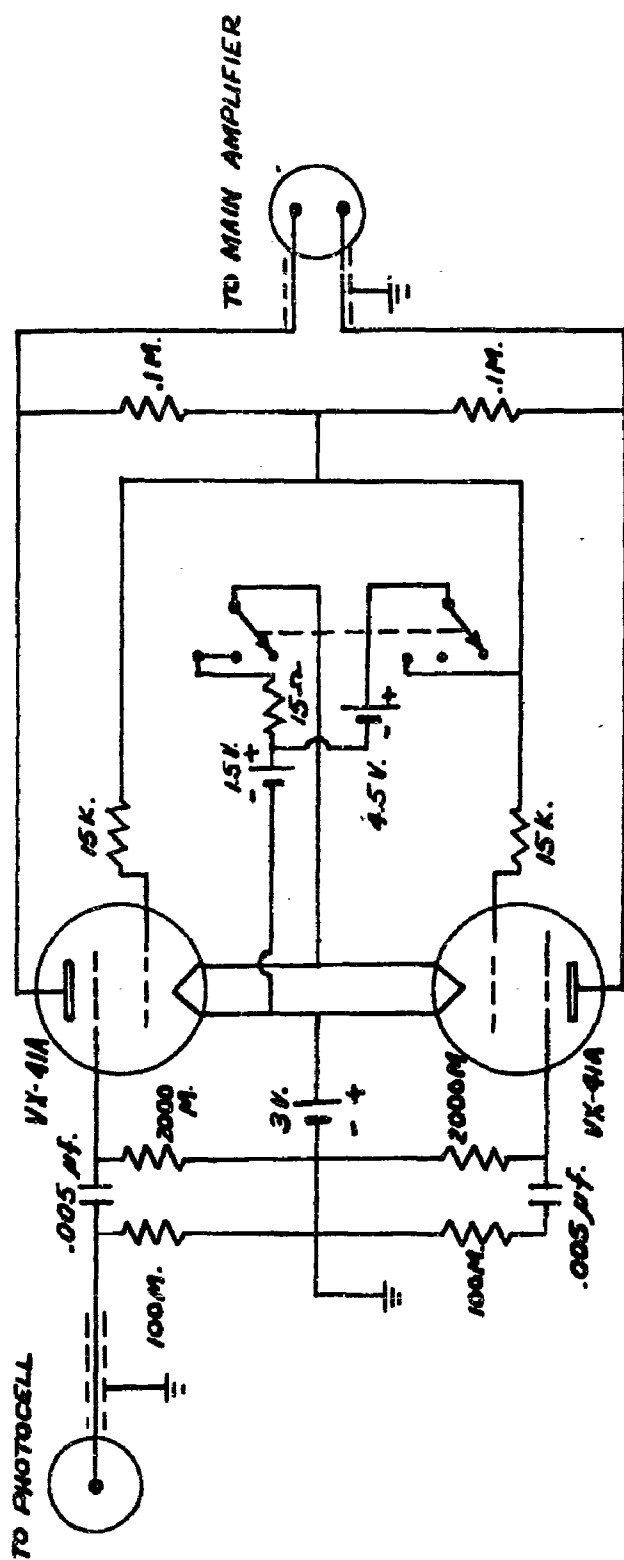
The light energy from the A-H6 lamp was reflected and focused onto the entrance slit of the monochromator by means of front surface plane and spherical mirrors. Directly in front of the entrance slit was mounted a light chopper consisting of a toothed aluminum disc rotated by a synchronous motor. The chopping rate was fixed at 33.3 cycles per second. The light coming out of the exit slit of the monochromator was reflected and focused by an optical system, similar to the one at the input, onto the cathode of the photocell.

The photocell was mounted in a polystyrene support in order to minimize leakage currents. The support and tube were completely shielded by a .035 inch thick iron box having a small opening in one end to allow the light from the monochromator to fall on the photocell cathode. The dry cell batteries used as accelerating potential between cathode and anode were also located within the shielding box in order to reduce the possibility of stray pickup.

Amplifier and Detector

Since the photoelectric yield when the titanium cathode was excited by essentially monochromatic light was rather small, it was necessary to amplify the signal from the photocell before applying it to a detecting device. Using a light chopper results in an alternating photocurrent signal and thus permits the use of an a.c. amplifier thereby eliminating the problems of d.c. amplification.

The photocell output is fed through a pre-amplifier to the main amplifier. The pre-amplifier serves as an impedance matching device to prevent loading down the high impedance photocell which would be the case if it were connected directly to the much lower impedance main



NOTE: M. = MEGOHM
K. = KILOHM

PRE-AMPLIFIER

FIGURE 4

amplifier input. The pre-amplifier, shown schematically in Figure 4, uses two Victorcon VX-41A high input impedance electrometer tetrodes and gives a gain of only $1/2$. It is battery powered, completely shielded, and shock-mounted to minimize the effects of microphonics.

The main amplifier consists of a high gain, narrow-band, balanced amplifier employing a "Parallel-T" null feedback circuit. A schematic diagram of the amplifier is shown in Figure 5. Two 60 cycle "Parallel-T" rejection filters in the plate circuit of the input stage block any 60 cycle pickup which may be presented to the input of the amplifier from the photocell or pre-amplifier. These filters have very good rejection properties at the tuned frequency. The ones employed for this experiment were measured as having a 60 db. attenuation at the desired frequency. Variable resistors were provided in two arms of the "T" to facilitate peaking the units. The input stage employs type 1280 tubes, more rugged versions of conventional 12SJ7's, in order to reduce microphonics. The 33.3 cycle networks provide inverse feedback from the plates to grids of the third stage for all frequencies except 33.3 cycles, thus the degeneration suffered by all other frequencies produces the effect of peaking the network tuned frequency. These networks are similar to the 60 cycle units and are tuned in the same manner. The attenuator at the grids of the second stage prevents overloading on strong signals, and in conjunction with the 8-step attenuator at the output of the third stage, make possible output readings over a 10,000 to 1 (80 db.) range of input voltages.

Measurements made on the amplifier indicated a bandwidth between half-power points of approximately $1/2$ cycle, and at frequencies 1.5 cycles above and below the center frequency the response was down 12 db.

The response dropped off more than 60 db. at 60 cycles, rose about 20 db. at higher frequencies, and then fell gradually off due to the .005 micro-farad capacitors shunting the plates of the second stage. The response below 33.3 cycles dropped off due to the feedback networks and coupling capacitor limitations. Thus, the narrow-band operation of the amplifier provides exceptionally good noise rejection characteristics. The maximum gain through the amplifier alone measured at 33.3 cycles is 250,000 for a sine wave input.

The amplifier is operated from two separate voltage regulated power supplies, one supplying plate and screen potentials and the second filament power. It was found necessary to operate the filaments in series from a d.c. source to eliminate heater-to-cathode hum which otherwise is severe.

The balanced output of the amplifier is fed to the grids of a balanced phase sensitive detector, shown schematically in Figure 6, whose common cathodes are "gated" by an auxiliary 33.3 cycle rectangular wave. This auxiliary signal is obtained from a type 927 gas phototube mounted on an arm at the light chopper and excited by an incandescent lamp supported by the same arm but located on the opposite side of the chopping wheel. Thus, the auxiliary signal is interrupted at the same rate as the primary light signal. A screw adjustment permits rotation of the arm about the periphery of the wheel thereby allowing control of the relative phase of the main and auxiliary signals. The auxiliary signal is amplified and shaped into a sharp rectangular wave before being applied to the detector cathodes. This cathode gating action allows only in-phase signals of the same frequency as the gating pulse to cause current to flow in the detector plate circuit, the detector

tubes being cut-off in the absence of the gating pulse. This current, after rectification by the tube and filtering by the large capacitors in the plate circuit, activates a 0-25 microamperes d.c. meter. Thus, the phase sensitive detector increases the selectivity of the overall system and hence improves the signal-to-noise ratio.

The designs of the pre-amplifier, amplifier, and phase sensitive detector, with exception of the power supplies, were taken from Tyler¹¹, the amplifier being a modified version of an earlier design by Roess¹².

2. Operation and Measurements

A diagram of the complete experimental setup is pictured in Figure 7. In order to eliminate the possibility of scattered light from the mercury arc exciting the photocathode and thus causing inaccurate current readings, the path of the monochromatic beam from the exit slit of the monochromator to the photocell was provided with a light shield. This also overcame the difficulties of ambient light interference and made the use of a dark room unnecessary.

It was originally intended to make use of the isochromatic method of plotting the Fowler curves and thereby eliminate the necessity of making an intensity spectrum calibration of the light source. Readings of relative photocurrent were observed for Tube I as a function of temperature, at several different frequencies in the neighborhood of ν_0 , for the range extending from 300 degrees K. to 650 degrees K. and the results plotted in the form $\log(I/T^2)$ as a function of $\log(1/T)$. The data proved useless since the plots resulted in straight lines. Thus, our results fell on the straight portion of the theoretical curve, the possibility of which was mentioned earlier, and it was

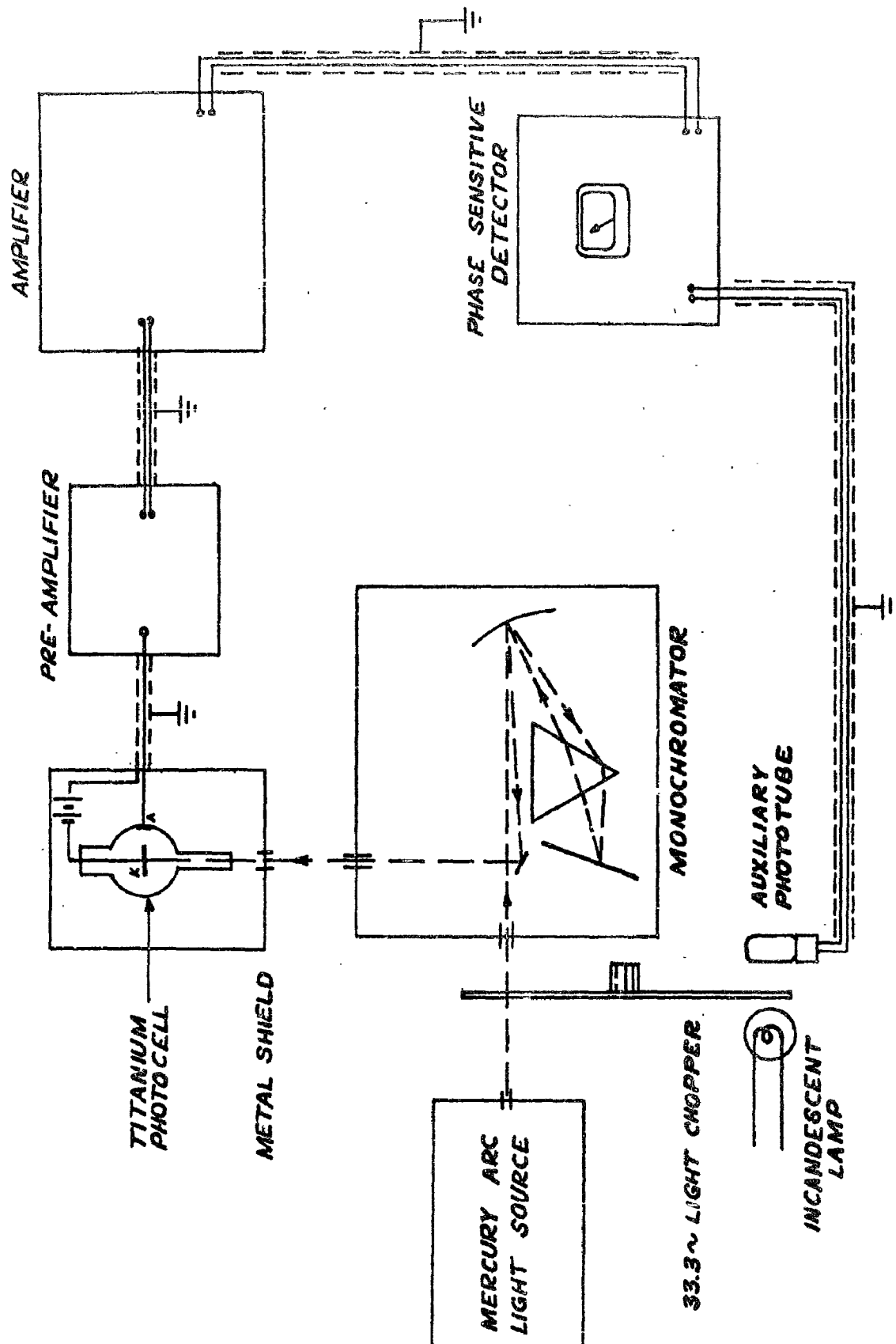


FIGURE 7

necessary to extend photocurrent measurements to higher temperatures in order to secure fruitful data.

When attempts were undertaken to obtain photocurrent readings at higher temperatures, it was found that violent fluctuations of current began to exhibit themselves at approximately 750 degrees K. and became more intense with increased temperature. The filament was heated from two 6 volt wet-cell storage batteries in parallel, completely enclosed in a heavy metal box with shielded wires connecting the battery box and the photocell shielding box; the entire shielding system was connected to earth through a heavy copper braid. Making the filament positive first with respect to the cathode and then the anode did not remedy the fluctuations, therefore the possibility that emission current from the heater to either the cathode or anode was causing the disturbance seemed unlikely. The likelihood that fluctuations in filament heat due to filament current changes could be the cause was also ruled out since the heat transfer from filament to cathode was relatively inefficient. Since time did not permit further investigations in this direction, the source of trouble was not determined.

Thus, the isochromatic method was abandoned in favor of the isothermal, or conventional Fowler method. To this end, readings of relative photocurrent were observed for Tube I as the incident light frequency was varied from 2800 Å to 2450 Å for seven different cathode temperatures ranging from room temperature to 571 degrees K. Temperature data was obtained by connecting the cathode thermocouple to a Leeds and Northrup Typo 8657-C Double Range Potentiometer Indicator whose readings were converted into temperature by means of a standard conversion table for chromel-alumel thermocouples. Approximately

250 volts d.c. was provided as accelerating potential for the photocell by means of dry cell batteries. It was necessary to use this high value of accelerating potential in order to prevent the tube from operating in the space charge limited region.

The spectral intensity of the light source was calibrated using a type 935 phototube [#] in conjunction with the narrow-band amplifier, an oscilloscope being employed as an output indicator. These measurements were taken immediately after the completion of the titanium photocell runs. The calibration curve for the 935 is shown in Figure 8 while the resulting spectral intensity distribution curve for the A-H6 mercury arc covering the range from 3200 Å to 2400 Å is shown in Figures 9 and 9a.

It was discovered that unfortunately the intensity of the A-H6 is not continuous, as far as our measurements are concerned, throughout this entire range. As Figure 9 indicates, a "hole" in the spectrum exists from about 2610 Å to 2510 Å. It was found that the intensity in this region was too low to give usable readings from either the 935 or the titanium photocell. A strong line is present in the low-pressure mercury spectrum at 2536 Å and it is believed that an absorption effect takes place at high pressures due to this line.

Since for Tube I readings of photoemission were required for frequencies extending through the "hole", it was necessary to take readings on both sides of the region and extrapolate this range as will be explained later. For Tube II, this procedure was not required since the response began to rise at longer wave-lengths and sufficient

[#] Obtained from and calibrated by R. W. Engstrom, RCA Special Tube Division, Lancaster, Pa.

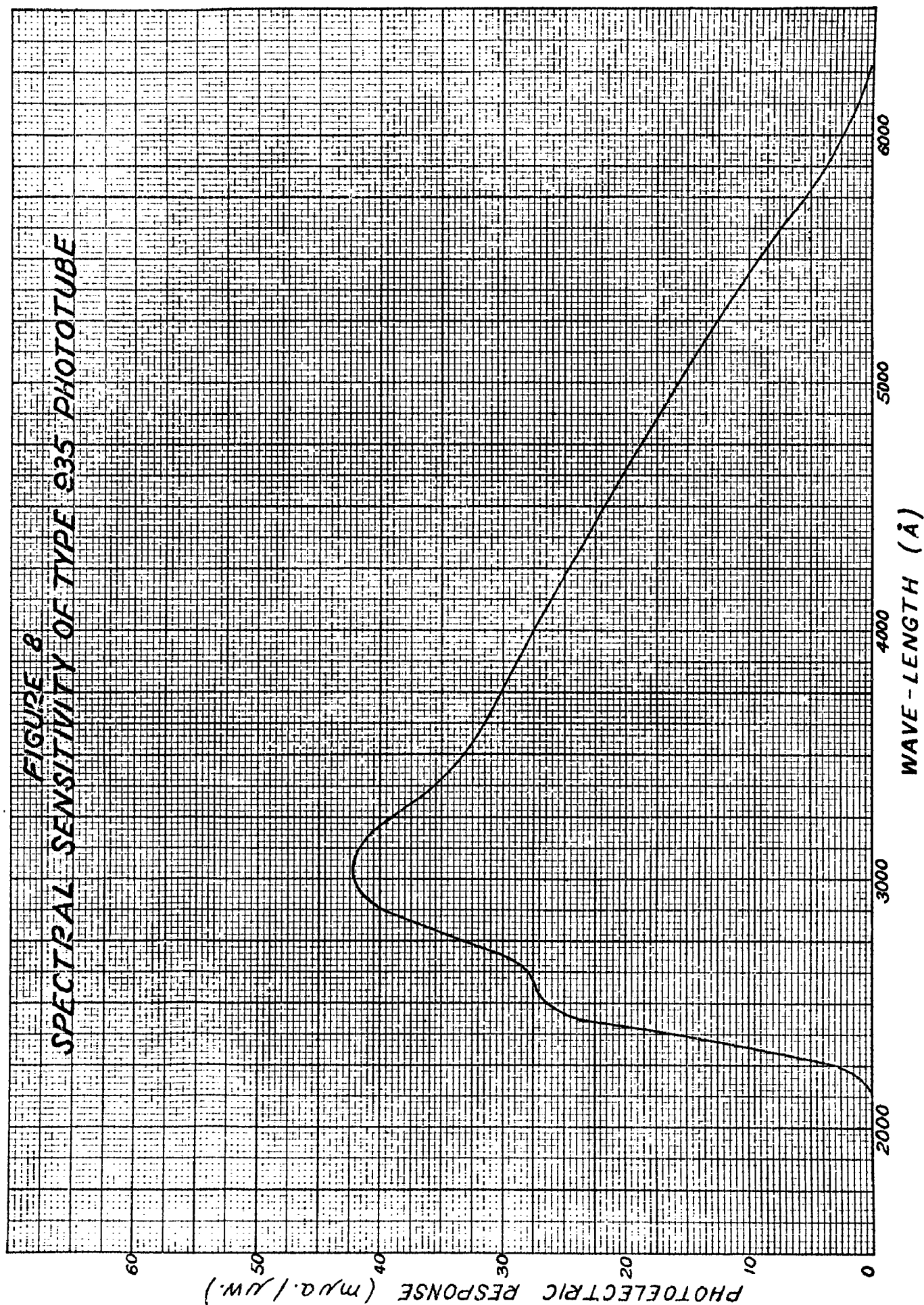


FIGURE 9
SPECTRAL INTENSITY CALIBRATION OF
A-H₈ MERCURY ARC

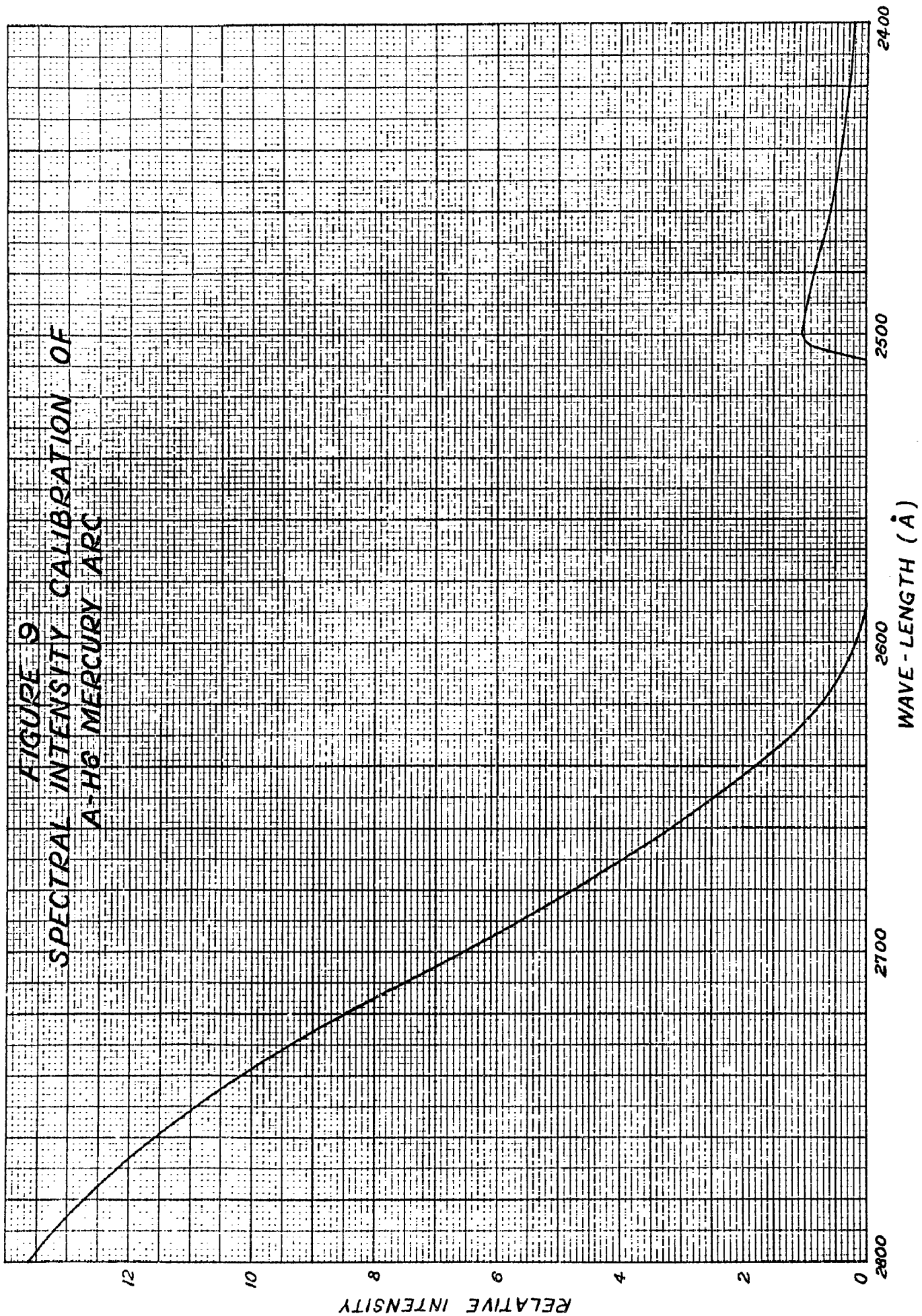
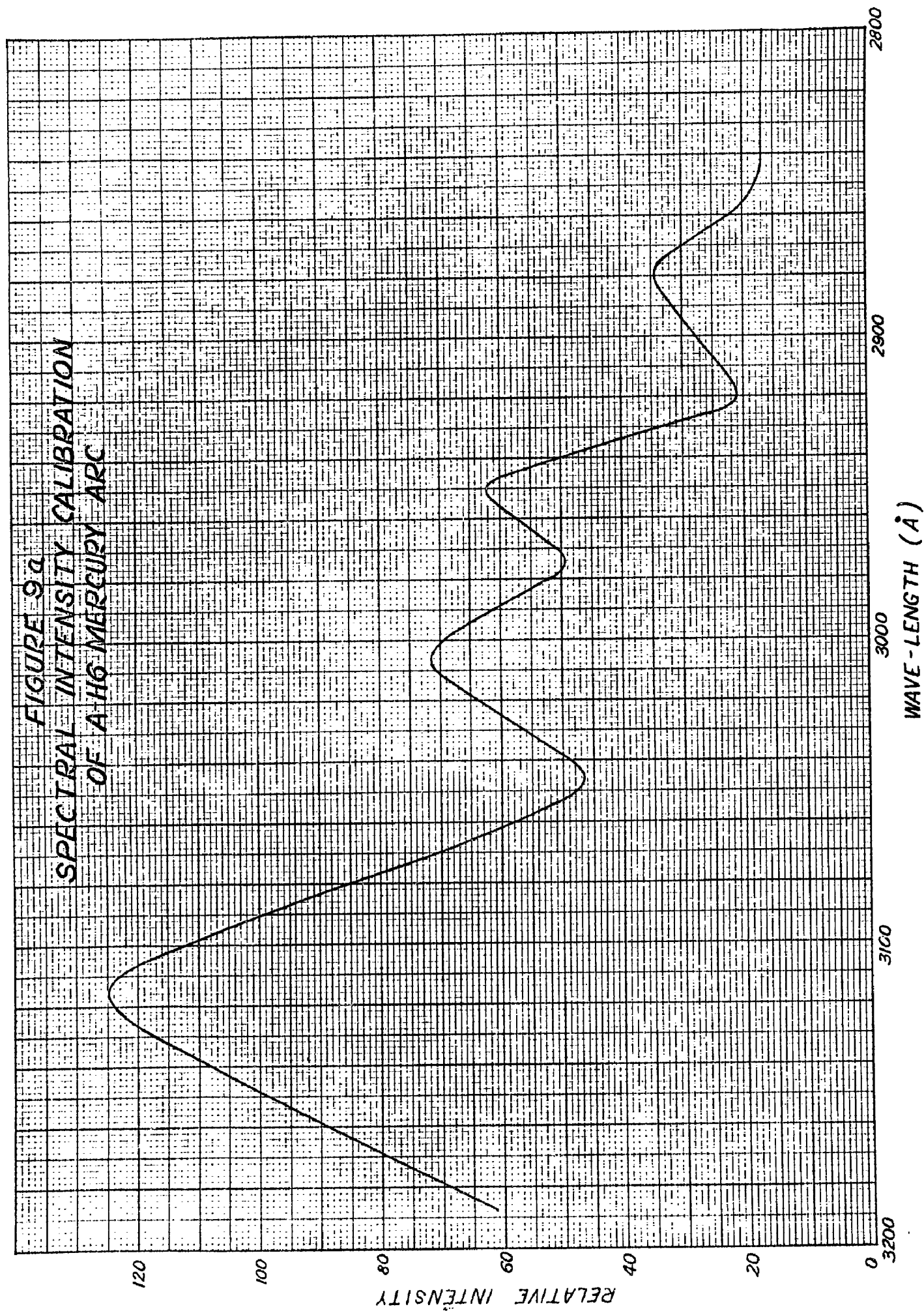


FIGURE 9a
SPECTRAL INTENSITY CALIBRATION
OF A Hg MERCURY ARC



data could be taken before reaching the void region.

No attempt was made to obtain photocurrent versus temperature readings for an isochromatic plot since its heater was not capable of producing the necessary high cathode temperatures. Instead, relative photocurrent values as a function of incident light frequency were observed for temperatures extending from room temperature to 102 degrees C. in the same manner as outlined for Tube I in order to secure data to prepare conventional Fowler plots. Due to different tube geometry, only 100 volts were required as accelerating potential for Tube II in order to draw saturation current.

IV EXPERIMENTAL RESULTS

1. Tube I

Due to the condition of low light intensity over the range of frequencies from 2610 Å to 2510 Å, it was necessary to provide some means of filling-in photocurrent data for this range. This was accomplished by plotting experimental values of relative photoelectric response as a function of wave-length for frequencies on both sides of the "hole" in the form of the familiar photoelectric response curve; Figure 10 depicts a typical curve for a run at room temperature.

It is evident from the figure that a smooth, accurate curve can be drawn through the experimental points enabling one to read off the values of relative response for the missing part of the spectrum. Also, the curve clearly shows that these values are needed to make a Fowler plot since the response curve begins to rise just before entering this part of the spectrum.

An alternative choice would be to make a Fowler plot directly from the experimental points and extrapolate the missing region directly. It was concluded that this method would lead to greater error since the experimental readings of photocurrent on the long wave-length side of the "void" were very small, therefore errors here would lead to much larger errors when logarithms are taken in the process of making a Fowler plot.

Figure 11 shows the Fowler plots resulting from the data for Tube I. All were found to give good fit with the theoretical curve. The original plots were made on a larger scale for greater accuracy and are shown in the appendix for reference. For convenience, \log_{10} of

FIGURE 10
TYPICAL PHOTOELECTRIC RESPONSE CURVE

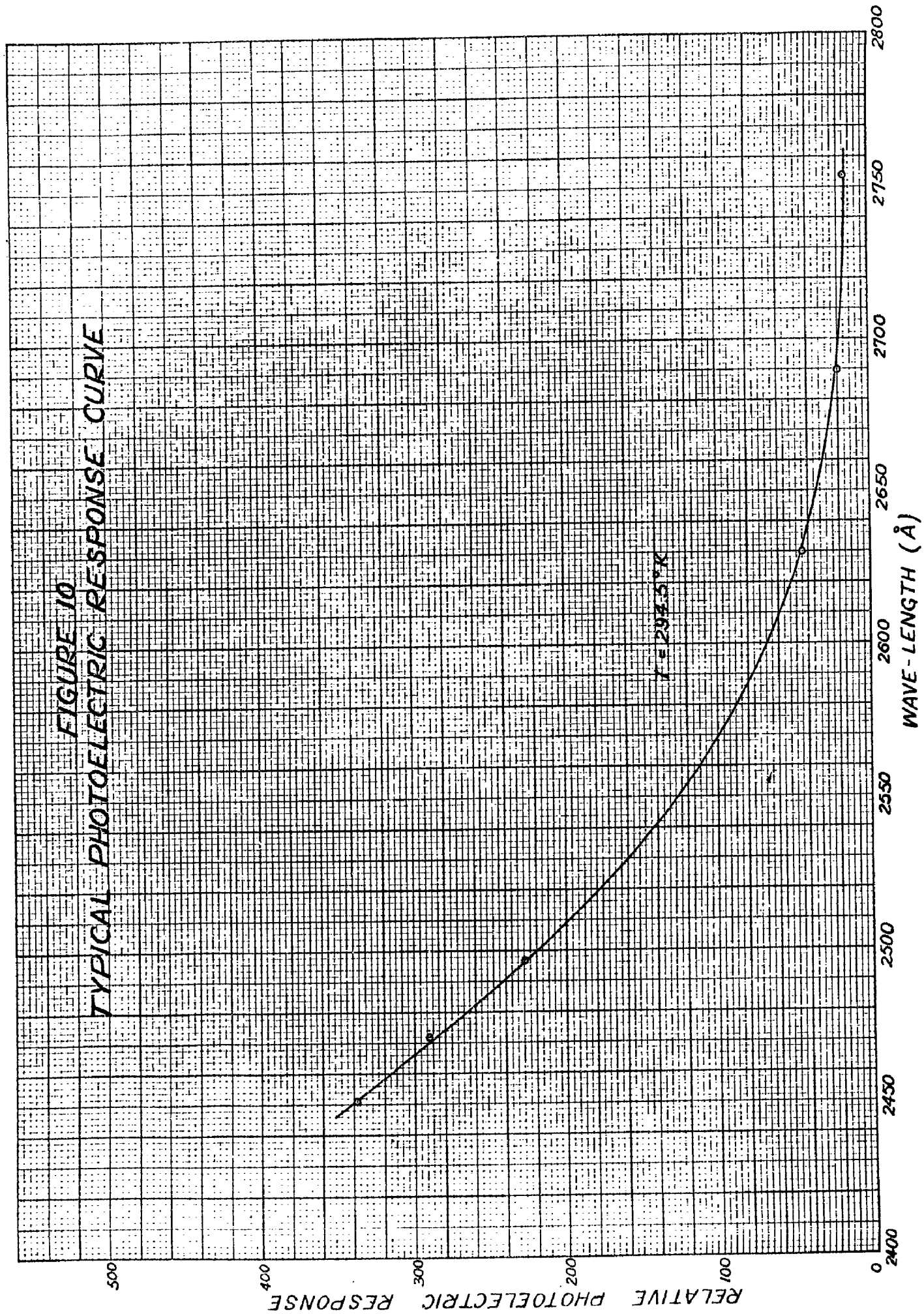
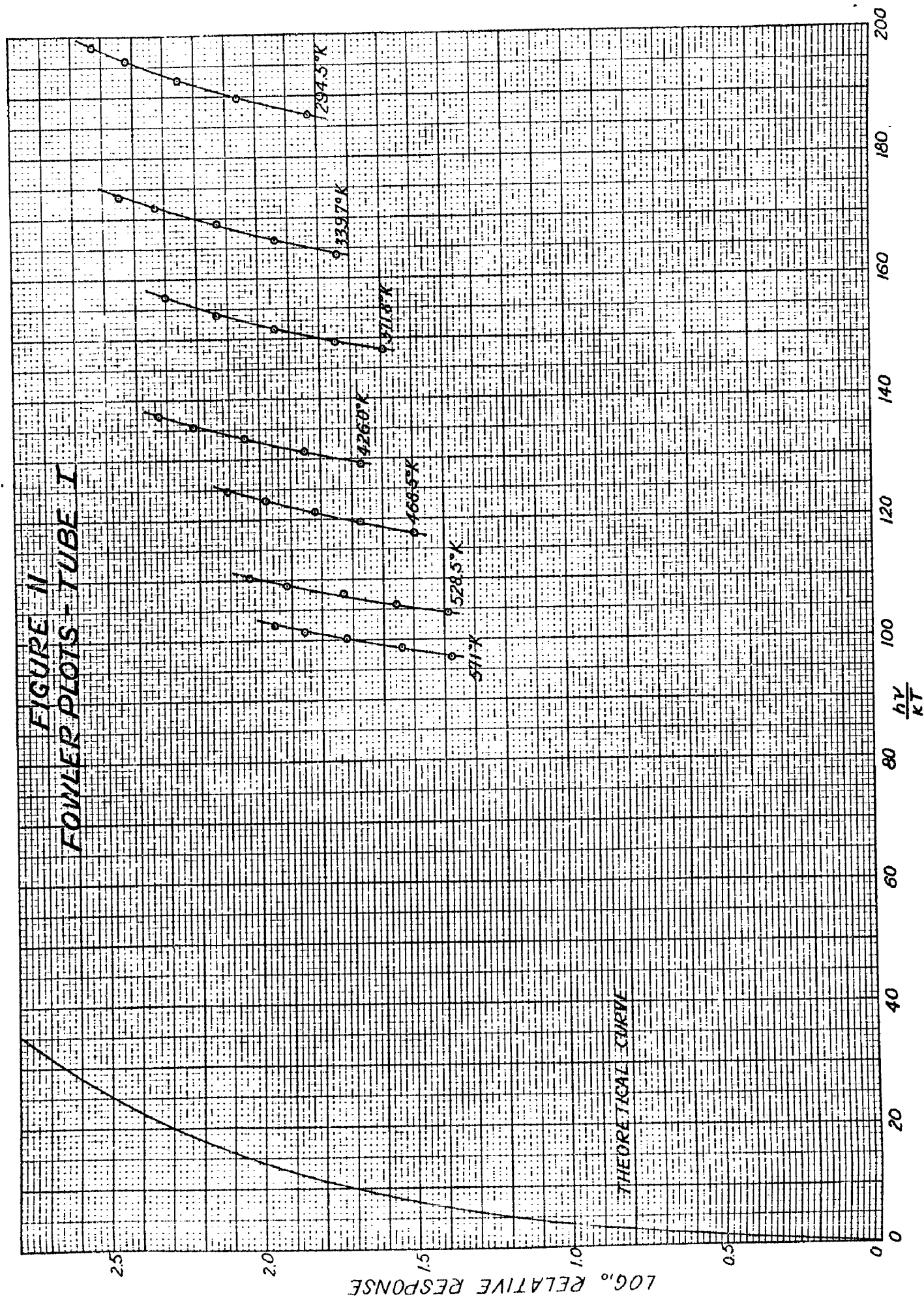


FIGURE II
FOWLER PLOTS - TUBE I



relative response was plotted as ordinates rather than $\log_{10} (I/T^2)$ since dividing by T^2 only affects B and produces a vertical shift which is unimportant.

Table I lists the graphical determinations of ϕ / kT , the horizontal shifts necessary to bring the experimental and theoretical curves into coincidence, and the values of ϕ calculated from these shifts. The mean value of work function is 4.50 volts with good consistency among the seven different runs, the maximum deviation from the mean being no greater than 1.5 % for any individual run.

2. Tube II

The photoelectric response for Tube II began to rise at about 3000 Å indicating a threshold near this point, therefore the "hole" region of the spectrum was not needed to secure sufficient photoemission data to construct Fowler plots. Thus, the extrapolation process employed for Tube I was unnecessary and the relative response was plotted directly in the form of Fowler curves. The resulting Fowler plots for Tube II are shown in Figure 12 where again \log_{10} of relative response was plotted as ordinates. All gave good coincidence with the theoretical curve when shifted. The original larger scale plots used in determining ϕ / kT are shown in the appendix for reference.

The results of Tube II are listed in Table I in the same form as described for Tube I. The resulting mean value of work function is 4.11 volts with maximum deviation from the mean being within ± 1 % for the four different temperature runs.

FIGURE 12
 FOWLER PLOTS - TUBE II

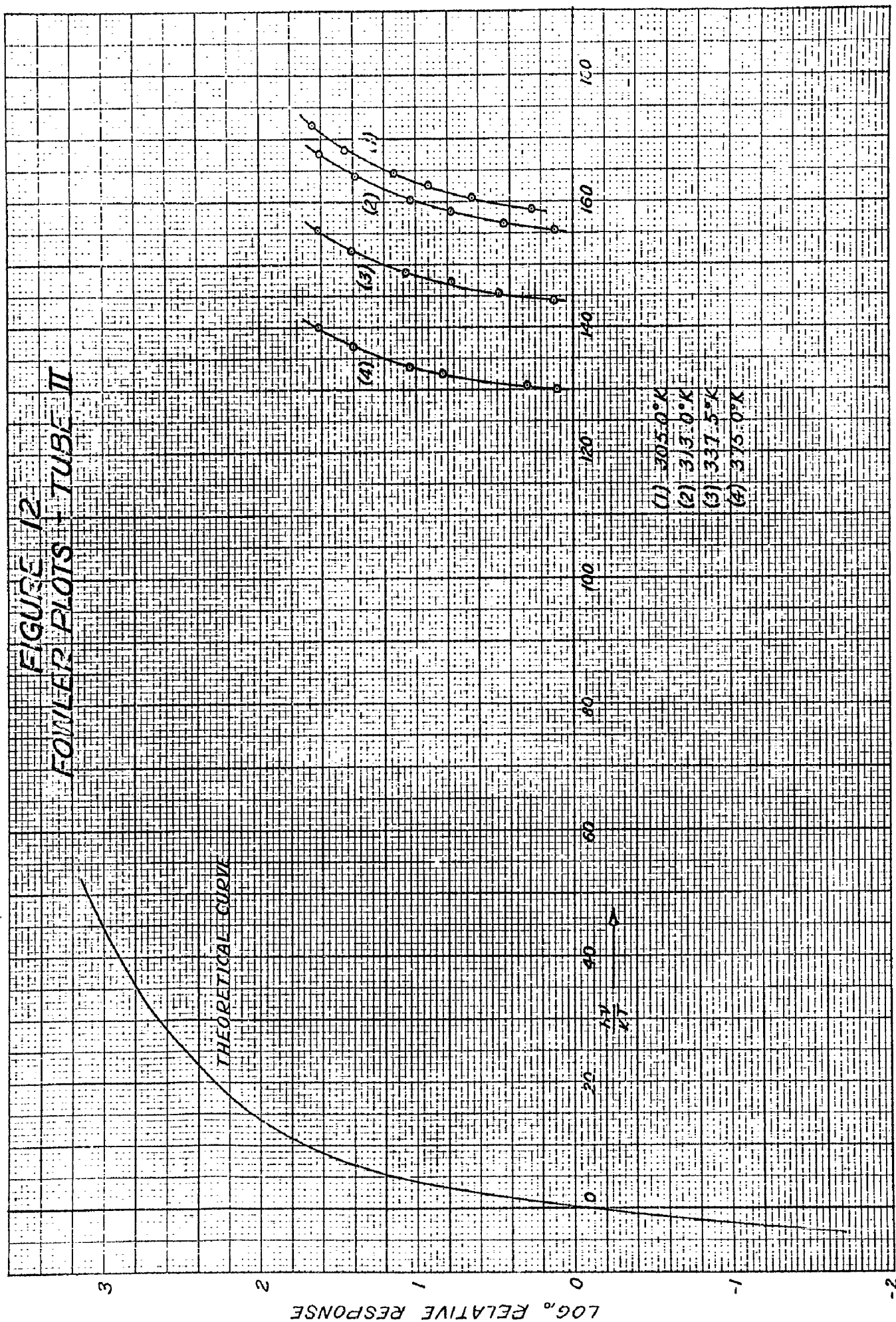


TABLE I
Results of Tube I

| T (deg. K.) | ϕ / kT | ϕ (volts) |
|-------------|-------------|----------------|
| 294.5 | 178.1 | 4.49 |
| 339.7 | 156.6 | 4.56 |
| 371.8 | 141.1 | 4.49 |
| 426.0 | 123.1 | 4.47 |
| 468.5 | 111.0 | 4.46 |
| 528.5 | 99.4 | 4.50 |
| 571.0 | 92.1 | 4.51 |
| | | 4.50 Mean |

TABLE II
Results of Tube II

| T (deg. K.) | ϕ / kT | ϕ (volts) |
|-------------|-------------|----------------|
| 305.0 | 155.9 | 4.07 |
| 313.0 | 153.5 | 4.12 |
| 337.5 | 142.2 | 4.11 |
| 375.0 | 129.0 | 4.14 |
| | | 4.11 Mean |

V SOURCES OF ERROR

One source of error is the result of assuming that the reflectivity of titanium does not vary with frequency, and therefore that the ratio of absorbed to incident energy remains constant. This is not strictly true since the reflectivity of titanium does vary slightly with frequency, however since the range of frequencies employed is comparatively limited, it is reasonable to assume that this error is minor.

A second source of error is due to an inherent property of the A-H6 lamp used as a light source. The quartz lamp envelope slowly changes its absorption characteristic as it ages in operation and tends to increase its ultra-violet absorption with increased time. Thus, the intensity spectrum calibration is inaccurate if taken at too long a time interval from the photocurrent measurements. Ideally, the two should be taken simultaneously. Since the intensity spectrum calibration was taken immediately after photocurrent measurements, this error is not serious. Intensity spectrum runs taken several hours apart also substantiated this belief since they showed only a slight change for this time interval.

A third source of error applying only to the results of Tube I is due to the "hole" existing in the mercury arc intensity spectrum thereby preventing direct measurement of photoelectric emission for this band of frequencies. However, judging from the consistency of the results, the extrapolation process described previously for filling-in this data seems to produce good accuracy.

VI CONCLUSIONS

The discrepancy between the two mean values of ϕ obtained from Tube I and Tube II might appear to be serious, however there is good reason to believe that the mean value of 4.11 volts obtained from Tube II is a good determination of the photoelectric work function of pure titanium while 4.50 volts, determined from Tube I, is the value of ϕ for a slightly contaminated titanium surface.

The former conclusion is supported by two facts; first, more care was exercised in the preparation of Tube II, especially during the pumping and baking stages, and second, Rentschler and Henry² obtained a value for the photoelectric work function of pure titanium using different photocell preparation and measurement techniques which is in excellent agreement with the results of Tube II. By extrapolating the conventional photoelectric response curve measured for titanium to zero response, they obtained the value of 2975 Å as the apparent threshold at room temperature for pure titanium, resulting in a value of 4.13 volts for ϕ .

The reason for believing that the titanium cathode of Tube I was slightly contaminated is that during the baking process while the tube was being pumped, the cathode was heated by means of passing current through the heater to a temperature of approximately 800 degrees C. by accident for about 15 minutes. Since titanium is very susceptible to contamination, it seems very likely that the cathode became slightly impure due to residual gases in the tube, the pressure at that stage being higher than its final value of 10^{-7} mm of Hg, and possibly also due to impurities given off by the heater. Rentschler and Henry¹³ also

observed that titanium , zirconium, and several other metals manifest a tendency towards increased work functions when a slight amount of oxygen combines with the pure metal.

Further evidence of the difficulty of preparing a photocell with a pure titanium cathode was demonstrated when Tube II was opened after completion of the measurements reported here in order to make structural changes. Photoemission measurements conducted on the tube after resealing indicated a lower work function, falling in the neighborhood of 3.85 volts. This was probably due to contamination of the titanium by the original getter deposit. The early version of Tube II mentioned in the construction section employing an aquadag inner coating and tantalum getters also resulted in a lower work function, ϕ for this case falling in the vicinity of 3.60 volts. This cathode was clearly contaminated since its removal showed a heavy brownish coating deposited on the titanium surface.

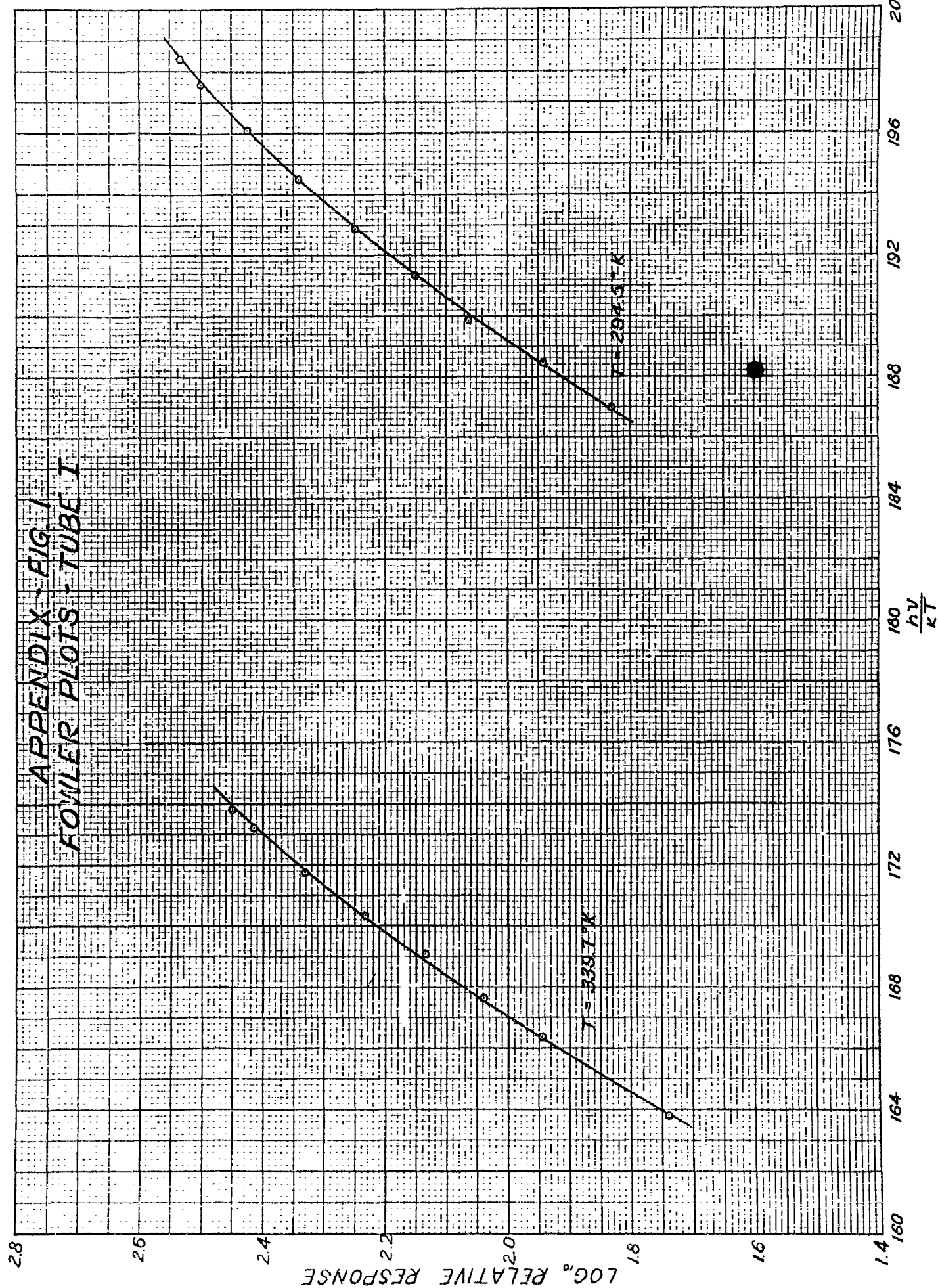
With these considerations in mind, the following conclusions can be drawn from the experimental results:

1. The photoelectric work function of pure titanium is 4.11 volts.
2. Contamination of the pure metal produces changes in the work function in either direction probably depending upon the type and amount of contamination suffered by the metal.

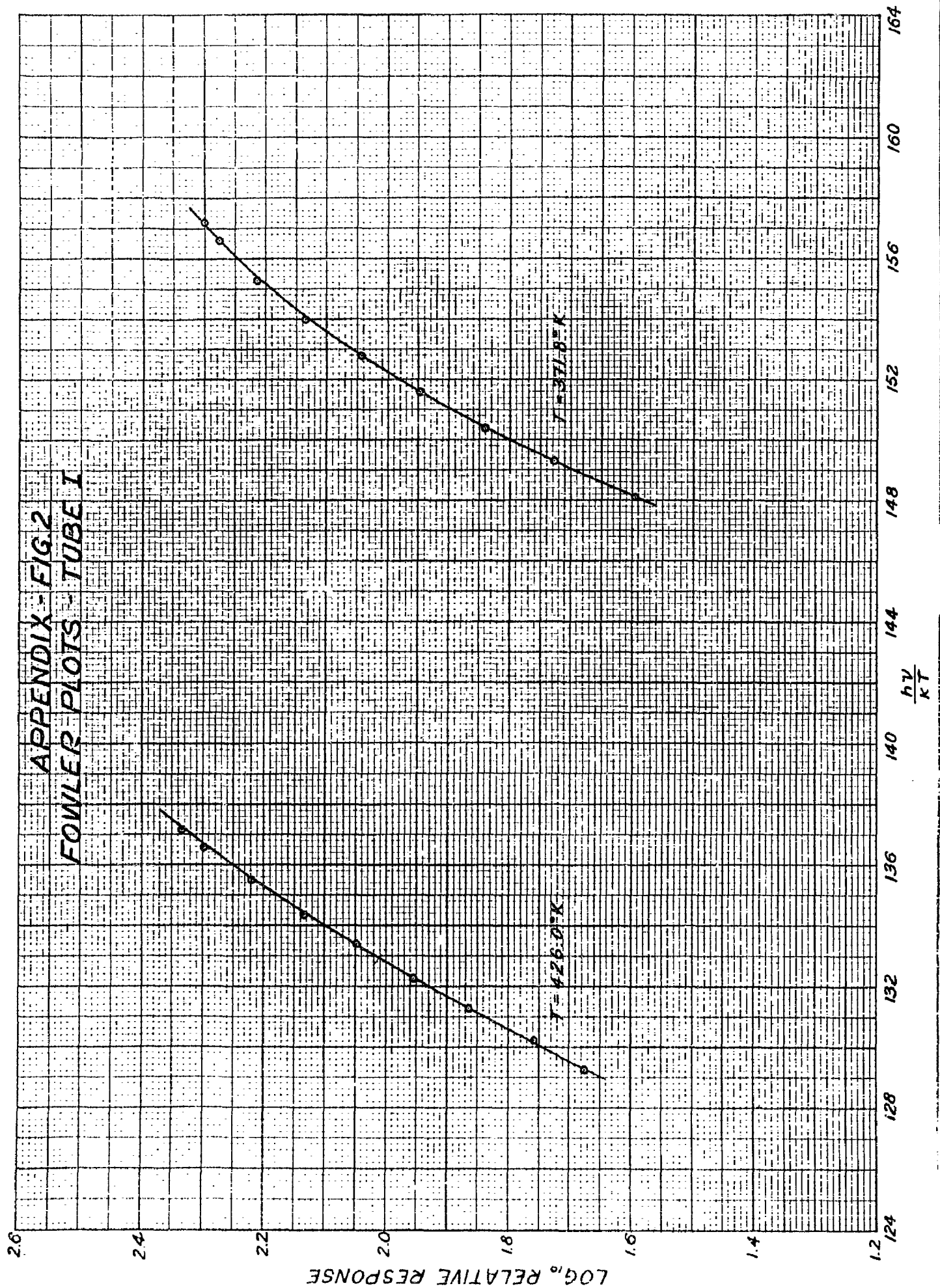
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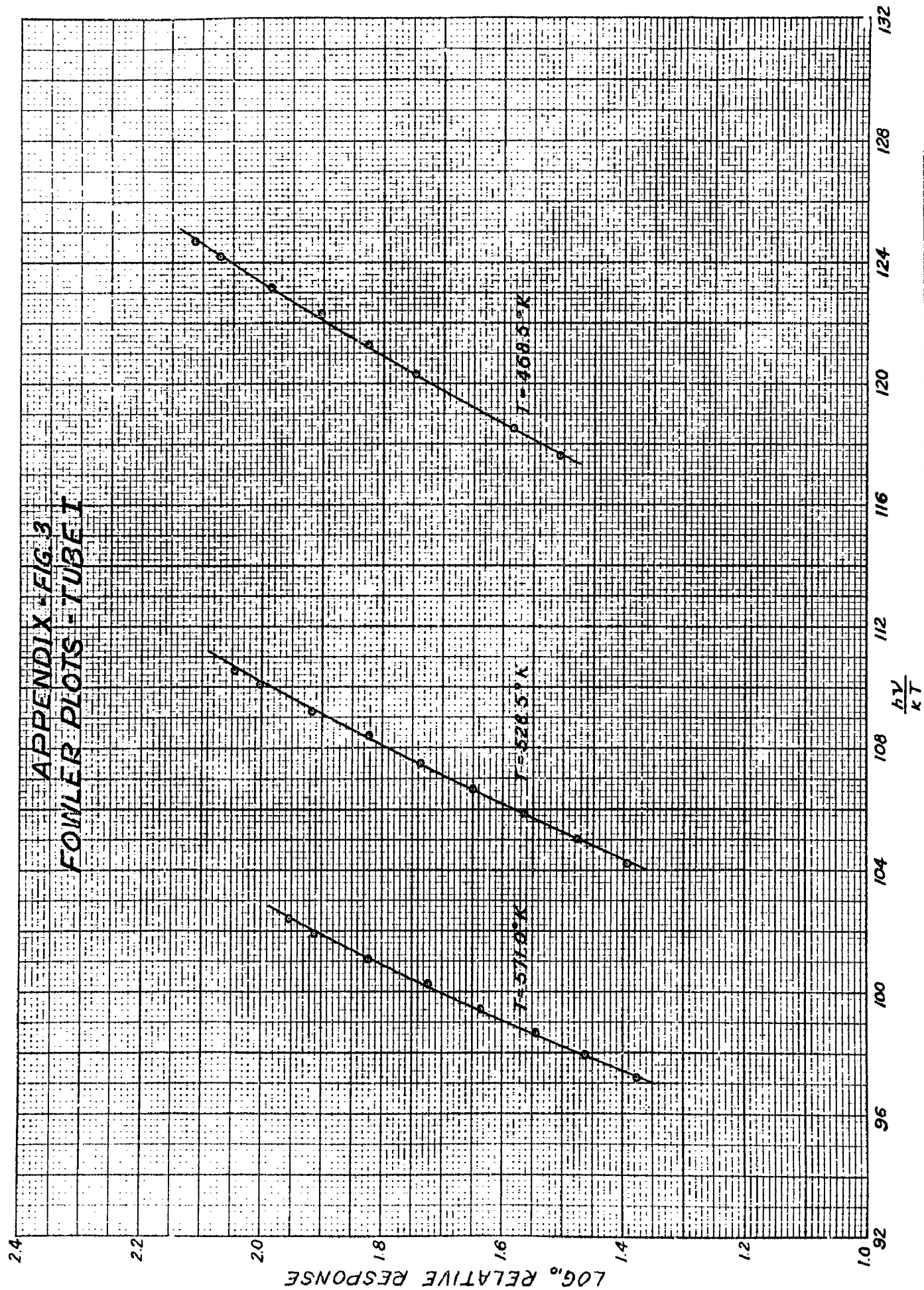
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APPENDIX - FIG. 1
FOVLER PLOTS - TUBE 1

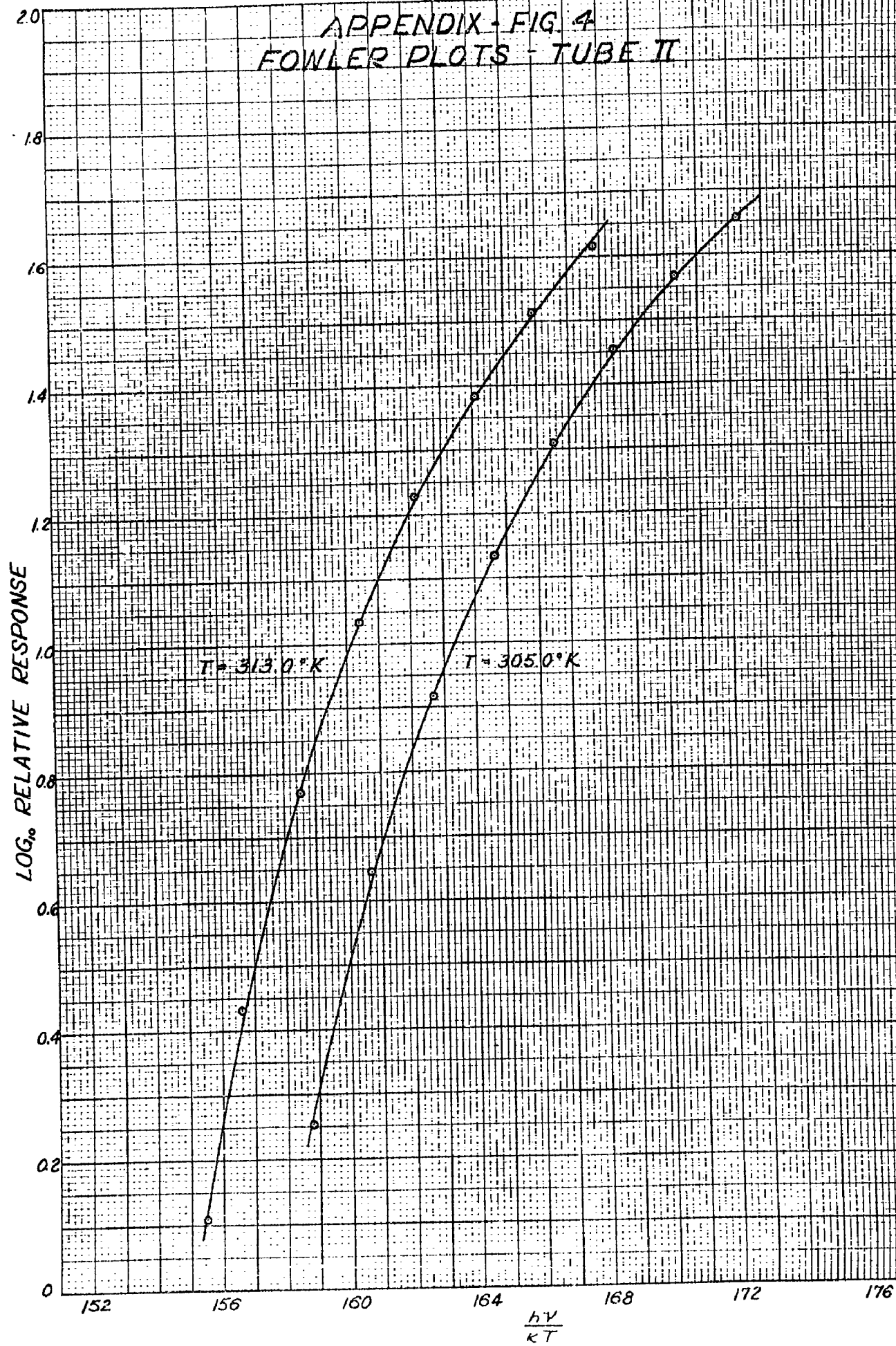


APPENDIX - FIG. 2
FOWLER PLOTS - TUBE I





APPENDIX - FIG 4 FOWLER PLOTS - TUBE II



APPENDIX - FIG. 5 FOWLER PLOTS - TUBE II

